Polarization-resolved photoluminescence study of individual GaN nanowires grown by catalyst-free molecular beam epitaxy

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Polarization- and temperature-dependent photoluminescence (PL) measurements were performed on individual GaN nanowires. These were grown by catalyst-free molecular beam epitaxy on Si(111) substrates, ultrasonically removed, and subsequently dispersed on sapphire substrates. The wires were typically 5–10 μm in length, *c*-axis oriented, and 30–100 nm in diameter. Single wires produced sufficient emission intensity to enable high signal-to-noise PL data. Polarized PL spectra differed for the $\boldsymbol{\sigma}$ and $\boldsymbol{\pi}$ polarization cases, illustrating the polarization anisotropy of the exciton emission associated with high-quality wurtzite GaN. This anisotropy in PL emission persisted even up to room temperature (4–296 K). Additionally, the nanowire PL varied with excitation intensity and with (325 nm) pump exposure time. [DOI: 10.1063/1.2206133]

Gallium nitride (GaN) nanowires grown by nitrogen-plasma-assisted molecular beam epitaxy (MBE) have been demonstrated to be III-V nitride structures of high crystalline quality and low defect density even when grown on lattice-mismatched substrates.[1–5] The nanowire morphology offers new embodiments of and applications for electronic and optical devices composed of single or few wires.[6,7] Recently, light-emitting diodes (LEDs) composed of dense as-grown arrays of nanowires exhibited increased light extraction efficiency and quantum efficiency compared to planar structures.[8] Study of nanowires also offers the opportunity to characterize material that has few, if any, defects with a volume of crystalline material that is comparable to the active volumes found in modern heterostructure devices. In this letter, we report the results of a polarized photoluminescence (PL) study of individual *c*-axis-oriented GaN nanowires grown by nitrogen-plasma-assisted MBE on Si(111) substrates. Temperature-dependent PL was performed in the $\mathbf{k} \perp \mathbf{c}$ geometry (pump light incident perpendicular to the nanowire axis) on wires that were dispersed onto sapphire substrates. The dependence of the excitonic transitions on the crystal symmetry in this high-quality wurtzite GaN led to emission spectra for the $\boldsymbol{\sigma}$-polarization case ($\mathbf{E} \perp \mathbf{c}$, polarization of luminescence perpendicular to nanowire axis, $\mathbf{k} \perp \mathbf{c}$) that differed from those observed with the $\boldsymbol{\pi}$-polarization case ($\mathbf{E} \| \mathbf{c}$, $\mathbf{k} \perp \mathbf{c}$) over the temperature range of 4–296 K. Details of the spectra varied from wire to wire, but, in general, spectral peaks associated with free and bound exciton peaks of strain-free GaN were readily identified. The PL spectra also depended on excitation intensity and duration of exposure to the 325 nm pump light.

Nanowires were grown on Si(111) substrates using conventional MBE equipped with elemental Ga and Al sources and a nitrogen plasma source.[4] An AlN buffer layer of roughly 50 nm was grown prior to switching to GaN growth. Nanowires were observed to spontaneously grow out of a highly defective GaN "matrix" layer that was a few micrometers thick; no separate metal catalyst particles were used to nucleate nanowire growth. The wire separations were typically 50–200 nm, diameters were typically 30–100 nm, and wires were up to 10 μm long. This length appears to be limited only by the growth time. In most instances, wire diameters were uniform over the entire length with cross sections displaying a well-formed hexagonal growth habit with sides conforming to the $\{10\bar{1}0\}$ prismatic planes.

For optical studies, the nanowires were dispersed onto sapphire plates after being removed from their growth substrates by ultrasonic agitation in an organic solvent. A photolithographically defined, indexed metal grid was placed over the dispersed wires to aid in the identification and location of individual wires. The mounted nanowire samples were then placed in a continuous-flow cryostat that enabled close optical access, and stable sample temperatures from 2.8 to 296 K. Samples were excited with a continuous-wave HeCd laser operating at 325 nm (3.815 eV) that was focused with a singlet lens to a spot diameter of 4 μm. PL spectra were collected with a 0.5-m monochromator that dispersed the photoluminescence onto an UV-sensitive photomultiplier tube. The nanowires mounted in the cryostat were imaged indirectly in phase contrast and their axial orientation was determined. Simultaneous imaging of the diffraction pattern of the pump light from a nanowire (or closely spaced group of parallel wires) under test was also used to confirm the position and orientation of a particular wire or group. Optical imaging could not resolve closely spaced wire pairs. Field emission scanning electron microscopy (FESEM) was used independent of the optical setup to image the samples of interest. With the wire axial orientation determined, an UV polarizer placed at the entrance slit of the monochromator was then oriented to select PL conforming to either the $\mathbf{E} \perp \mathbf{c}$ or $\mathbf{E} \| \mathbf{c}$ case. The absolute spectral accuracy of the monochromator was within 0.4 meV of several atomic reference lines that overlapped the wavelength range of interest.

Polarized and unpolarized PL spectra were collected from several dispersed nanowire samples. Strong near-band-edge emission occurred within 1 meV of energy peaks associated with both free and bound excitons of strain-free GaN at low temperatures (<5 K).[9] The relative strengths and linewidths of these peaks varied from wire to wire and with excitation intensity. In a few cases, the spectral peaks fell as

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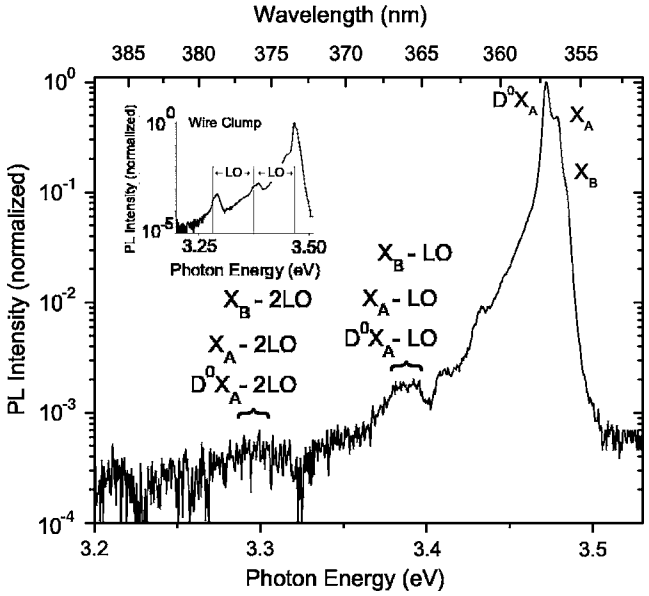

FIG. 1. Low-temperature (3.2 K) PL spectrum of a B738 GaN nanowire pair (5.7 μm in extent) taken without a polarizer. X_A—A free exciton, X_B—B free exciton, D^0X_A—donor-bound A exciton, and LO—longitudinal optical phonon energy (~92 meV). Inset shows a polarization-insensitive PL spectrum for a clump of nanowires consisting of several wires. The signal-to-noise improvement enables an easier recognition of the phonon-replica peaks separated by the LO energy.

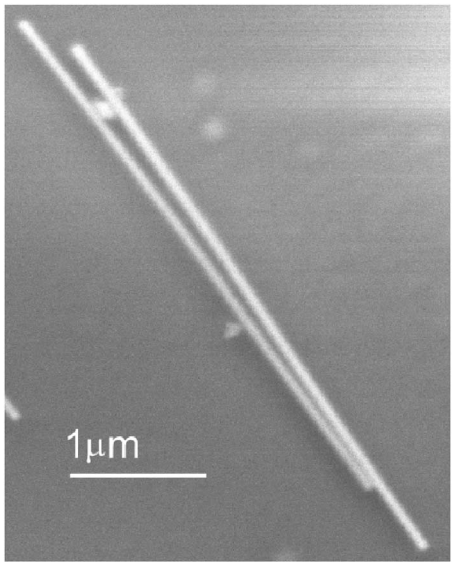

FIG. 2. FESEM image of the B738 GaN nanowire pair referred to in text and Figs. 1, 3, and 4. Scale bar indicates length of 1 μm.

much as 3 meV from the expected positions for strain-free GaN at low temperatures. More study is needed to determine whether these energy shifts are inherent to these particular wires or a result of strain introduced to these wires in the wire dispersal process.

Figure 1 shows the (unpolarized) 3.2 K PL spectrum of a 5.7-μm-long nanowire pair. The FESEM image of this wire pair appears in Fig. 2, and it shows their closely spaced parallel alignment. These wires came from the growth run labeled B738. The excitation intensity for the Fig. 1 data was 550 W/cm^2. The donor-bound exciton D^0X_A peak is observed to dominate the spectrum at the stress-free position of 3.472 eV.[9,10] The c-axis lattice constant (0.518 46±0.000 05 nm) for these wires, measured with x-ray diffraction, matched that of strain-free bulk GaN.[5] The linewidth of the D^0X_A peak (5 meV) is broader than that of typical strain-free GaN (~1 meV),[10] which is similar to observations made by Bae *et al.*[11] Free exciton peaks X_A and X_B are evident and, respectively, located at 3.478 and 3.483 eV. The first phonon replicas of these dominant peaks occur over the spectral range of 3.38–3.39 eV. Evidence of the second phonon replicas appears above the noise floor at around 3.29 eV. We observed better resolution of these peaks in the (unpolarized) PL spectra from wire samples composed of "clumps" of more than two randomly oriented wires. This is illustrated in the inset of Fig. 1. Other weaker peaks at 3.41, 3.34, and 3.21 eV appearing in Fig. 1 may arise from excitons bound to surface and or other structural defects.[9] The peak at 3.43 eV is not yet assigned but was also observed in nanowire samples taken from separate growth runs. Broad blue luminescence centered around 2.9 eV was observed in PL spectra taken from the B738 as-grown material (nanowires remaining on their growth substrate), while no such emission was observed in individual dispersed nanowires, or clumps of individual nanowires. This broad blue emission therefore arises from the highly defective GaN matrix layer portion of the growth.[5] Finally, no yellow luminescence (YL), which is widely reported to be associated with vacancy and structural defects in GaN films,[12] was observed in the PL of individual nanowires.

Recent spectroscopic studies of free-standing hydride vapor phase epitaxy (HVPE) grown wurtzite GaN have illustrated the polarization anisotropy of the photoluminescence that is inherent to this material.[10] Figure 3 shows polarization-resolved PL spectra from the same B738 nanowire pair shown in Fig. 2. PL spectra with $\boldsymbol{\sigma}$ and $\boldsymbol{\pi}$ polarizations recorded over a range of temperatures from 4 to 60 K are illustrated. The excitation intensity used for all of these spectra was 85 W/cm^2. Free exciton peaks X_A and X_B, as well as the donor-bound exciton peaks D^0X_A and D^0X_B, are visible to varying degrees in the spectra. As with the work in Ref. 10, the D^0X_A peak dominates the $\boldsymbol{\sigma}$ PL spectrum at low temperatures and it remains dominant up to 40 K, at which point the free exciton X_A peak begins to dominate. For the $\boldsymbol{\pi}$ polarization, the D^0X_B peak dominates at low temperature and remains dominant up to 40 K, where the free exciton X_B peak dominates the spectrum. These spectral differences between the two polarizations are partially explained by the dipole-forbidden nature of polariton generation from A excitons for the π-polarization case[10] and are expected in ideal wurtzite crystals (see Ref. 12, Chap. 10). Differences in the PL spectra between the $\boldsymbol{\sigma}$ and $\boldsymbol{\pi}$ cases remain observable even up to room temperature. Figure 4 illustrates the PL spectra for temperatures of 80–296 K with an excitation intensity of 550 W/cm^2. The emission peak for the $\boldsymbol{\sigma}$ case is consistently at lower energy than the peak observed for the $\boldsymbol{\pi}$ case over the full temperature range. At room temperature, the energy difference between these two peaks is 7 meV. The emission peak at 3.49 eV for the $\boldsymbol{\pi}$-polarization case at 80 K is assigned to the C free exciton X_C. The strength of the PL peak emission for this nanowire pair at room temperature is about 10% that measured at 4 K.

The dependence of single-wire PL spectra on pump intensity was also examined but was difficult to quantify due to transient effects associated with pump exposure times. Pump intensities were varied from 85 to 550 W/cm^2, and the PL

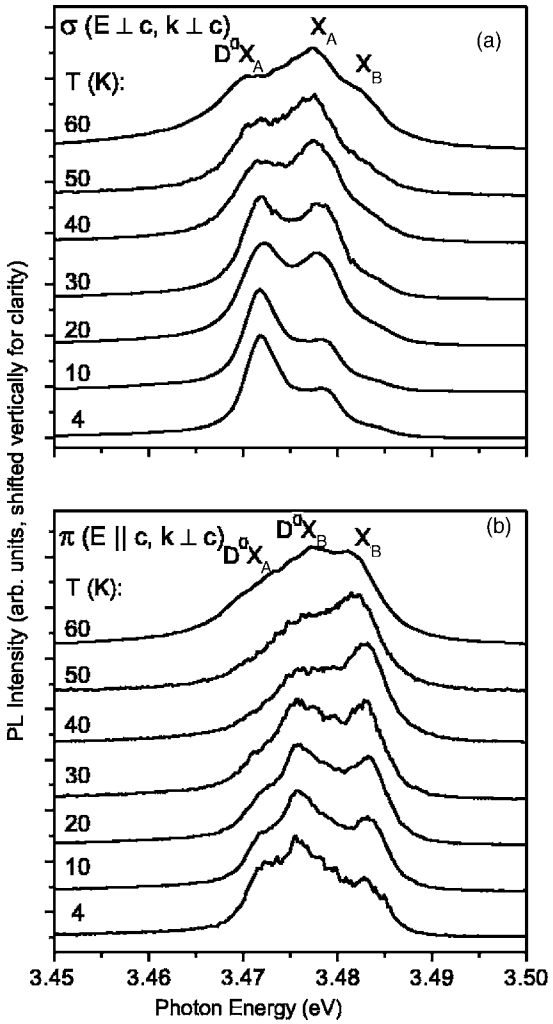

FIG. 3. Photoluminescence spectra of a B738 GaN nanowire pair for (a) σ and (b) π polarizations at different temperatures. The plots are normalized and shifted with temperature for clarity.

intensity generally increased with excitation intensity. The dominant D^0X_A peak at 3.472 eV remained dominant over this intensity range. However, the relative strengths of the lesser peaks due to the free excitons X_A and X_B (at 3.478 and 3.483 eV) also increased with excitation intensity, causing the D^0X_A peak to be less prominent at higher excitation intensities. In many instances extended exposure of the nanowires to the 325 nm pump light reduced the single-wire peak PL intensity. Given equipment constraints, PL scan times typically required 10 min or more, so it was not entirely possible to separate the effects of exposure duration from the effects of changes in temperature or excitation intensity. Exposure duration effects were minimized to some degree, however, by shuttering the 325 nm pump light between scans.

In summary, polarization-resolved photoluminescence was measured on isolated, GaN nanowires that were grown

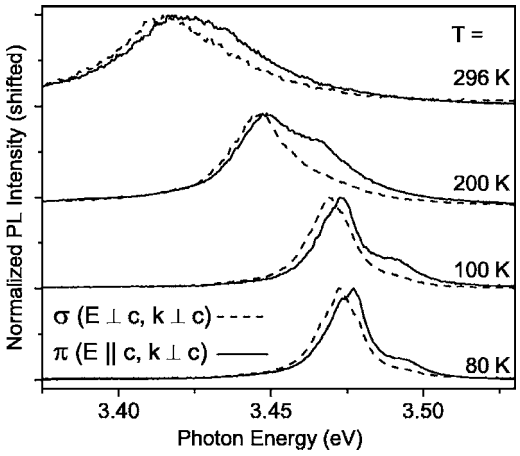

FIG. 4. Photoluminescence spectra of a B738 GaN nanowire pair for π (solid) and σ (dashed) polarizations at higher temperatures. The plots are normalized and shifted with temperature on the y axis for clarity.

by nitrogen-plasma-assisted MBE on Si(111) substrates. The PL spectra were easily resolved, exhibited high signal-to-noise ratios, and showed polarization anisotropy expected for strain-free wurtzite GaN from a temperature of 3.9 K all the way up to room temperature. PL spectra varied from wire to wire, but the variation was usually limited to the relative heights and spectral linewidths of the PL peaks. Transient behavior, associated with the duration of pump exposure, was also observed, and this effect made a quantitative examination of the pump intensity dependence of the PL difficult to ascertain. Further work is needed to isolate the effects of excitation intensity, light exposure, and nanowire sample preparation.

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